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An isothermal section and a ZrC-Ta polythermal section were constructed at 2273°K on the basis of data from radiographic, metallographic and chemical analyses and determination of the melting points of alloys of the Zr-C-Ta system and it was demonstrated that triple compounds do not exist in the system. In the solid state there are three single-phase fields -- $Zr_xTa_yC_z$, $(Ta, Zr)_2C$ and $(Ta, Zr)$; three two-phase fields -- $Zr_xTa_yC_z + (Ta, Zr)$, $(Ta, Zr) + (Ta, Zr)_2C$ and $(Ta, Zr)_2C + Zr_xTa_yC_z$; and the three-phase field -- $Zr_xTa_yC_z + (Ta, Zr)_2C + (Ta, Zr)$, that is, only phases existing in the corresponding double systems.

The creation of manufacturing refractory materials of the cermet type, in /318* which the carbides of transition metals, especially ZrC, serve as the refractory base, involves the study of the interaction of the mentioned carbide with a metal bond over a wide range of temperatures.

For example, data are available on the interaction and structure of the diagrams of state of the systems ZrC with Zr [1, 2], Nb [3], Mo [4], W [5], and also the results of study of contact interactions of refractory carbides, including ZrC, with transition metals [6].

This investigation was devoted to the study of the interaction of ZrC with Ta in a wide range of temperatures and concentrations**.

On the basis of the data in [8] it can be assumed that in the structure of alloys in the $Me^{IV}-C-Me^{V}$ systems we should observe a certain similarity, involving an identity of the position of the fields of multi-phase equilibrium, since the thermodynamic parameters, determining, according to [8], the onset of multi-phase equilibrium, are close for the indicated systems. Some corrections are introduced by the differences of the dimensional factors and the type of structure of the boundary systems $Me^{IV}-Me^{V}$. The marginal systems Zr-C [1, 2] and Ta-C [9, 10] have been investigated. The Zr-Ta system [11] differs from the Zr-Nb system [12], although data in [13] indicate that there is a similarity. The causes for the difference in the behavior of Nb and Ta in relation to Zr have been studied by Howlett in [14]. Whereas in the Ti-Nb [15] and Ti-Ta [16] systems the deformation energy of solid solutions is small and a full reciprocal solubility is observed, in the Zr-Nb and Zr-Ta systems, with higher

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*/Numbers in the margin indicate pagination of the original foreign text.
**The results of this study were reported in April, 1964, at the Scientific-Technical Conference of the Leningrad Technical Institute, imeni Lensovet [7].

maximum deformation energy values for the crystal lattice of the solid solution, a maximum appears for the immiscibility region. Since in the Zr-Ta sys- /319 tem the peak of deformation energy attains a maximum value, the immiscibility region in this system extends to the solidus line. Naturally, β-Zr and Ta will be in a solid state below the mentioned line; this in turn leads to the appearance of the field of three-phase equilibrium β-(Zr, Ta) + $Zr_x Ta_y C_z$ + (Ta, Zr) in the triple system Zr-C-Ta.

The presence of carbon in the ZrC and NbC and TaC compounds levels the difference in the behavior of Nb and Ta in relation to Zr in view of the formation of (Zr, Nb, Ta)-C bonds, close in strength, greatly exceeding the Zr-(Nb, Ta) bond strength. This is indicated by the formation of continuous solid solutions in the ZrC-NbC, ZrC-TaC systems [17, 18].

We prepared a number of alloys whose composition is given in Tables 1 and 2.

TABLE 1.

| Composition of the Alloy | Computed Data | | | | Results of Chem. Analysis | | | Regime of Thermal Processing at 2273°K (Hours) |
|---|---|---|---|---|---|---|---|---|
| | Ta | | C | | Ta | C Bound | C Free | |
| | Weight % | Atomic % | Weight % | Atomic % | | | | |
| $Zr...Ta_{0.017}C...$ | 3 | 0.91 | 11.25 | 49.54 | — | 11.14 | 0.2 | 2+1+ +1+1 +1+1··1 |
| $Zr...Ta_{0.030}C...$ | 5 | 1.52 | 11.02 | 49.24 | 5.06 | 11.0 | 0.1 | |
| $Zr...Ta_{0.061}C...$ | 10 | 3.12 | 10.45 | 48.44 | — | 10.24 | 0 | |
| $Zr...Ta...C...$ | 15 | 4.87 | 9.87 | 47.56 | — | — | — | |
| $Zr...Ta_{0.137}C_{0.873}$ | 20 | 6.78 | 9.28 | 46.61 | 19.87 | 9.23 | — | |
| $Zr...Ta_{0.199}C_{0.801}$ | 30 | 11.07 | 8.13 | 44.46 | — | — | — | |
| $Zr_{0.723}Ta_{0.277}C_{0.723}$ | 40 | 16.15 | 6.96 | 41.93 | — | — | — | |
| $Zr...Ta_{0.367}C_{0.633}$ | 50 | 22.48 | 4.81 | 38.76 | 50.3 | 4.72 | — | 2+2+2 |
| $Zr...Ta_{0.466}C...$ | 60 | 30.41 | 4.64 | 34.80 | — | — | — | |
| $Zr...Ta_{0.584}C_{0.416}$ | 70 | 40.33 | 3.49 | 29.83 | 69.90 | 3.55 | — | |
| $Zr...Ta_{0.699}C_{0.301}$ | 80 | 53.65 | 2.33 | 23.17 | — | 2.40 | — | |
| $Zr...Ta_{0.840}C_{0.160}$ | 90 | 72.40 | 1.16 | 13.80 | — | 1.20 | — | |

The initial materials for preparing the alloys was ZrC with a bound carbon content of 11.3%, 0.5% free carbon and 0.2% nitrogen, powdered tantalum (> 99.5%) and calcithermal and acetylene soot. Cylinders with d = 10 and h = 10 mm were pressed from the corresponding powders after careful mixing at a pressure of 4 tons/cm$^2$ and subjected to annealing at 2273°K on a ZrC support in a TVV-4 vacuum furnace at a rarefaction of about $2-5 \cdot 10^{-4}$ mm Hg. After 1-2 hours of exposure the samples were cooled and fractionated, and briquettes for a second

TABLE 2.

| Alloy | Composition of the Alloy | Computed Data | | | | Results of Chemical Analysis | | Regime of Thermal Processing at 2273°K (Hours) |
|---|---|---|---|---|---|---|---|---|
| | | Atomic % | Weight % | Atomic % | Weight % | Ta | C Bound | |
| | | 38 | | | 4.35 | — | 4.28 | |
| | | | | 23 | 2.40 | — | 2.43 | |
| | | | | 14 | 1.2 | 86.8 | 1.12 | |
| | | 10 | 57 | 33 | 3.41 | — | 3.35 | |
| | | 9 | 67 | 24 | 2.17 | 91.2 | 2.20 | |
| | | 7 | 78 | 15 | 1.21 | — | 1.28 | |
| | | 19 | 47 | 34 | 3.83 | 79.6 | 3.75 | 2 + |
| | | 35.5 | 35.5 | 29 | 3.48 | — | — | |
| | | 24 | 49 | 27 | 2.83 | — | 2.88 | |
| | | 10 | 85 | 5 | 0.37 | — | 0.50 | |
| | | 7 | 86 | 7 | 0.52 | — | 0.57 | |
| | | 14 | 70 | 16 | 1.36 | — | 1.31 | |
| | | 20 | 48.5 | 31.5 | — | — | — | |

annealing were again pressed from a powder ground to a particle size of less than 60 μ.

After each annealing we determined the lattice parameter of the forming solid solution. The state of equilibrium was considered attained if the subsequent exposure did not lead to a change of the lattice constant. The lattice constant decreases (Figure 1) due to both an increase of the concentration of defects in the C sublattice and to the introduction of Ta atoms, whose size is considerably less than the size of the zirconium atoms. It should be noted that the dependence of the change of the lattice parameter in the case of solution of tantalum in ZrC on the atomic percentage of tantalum is similar to the dependence in the case of solution of Nb in ZrC [3]. The reason for this is the equality of the Nb and Ta atomic radii ($r_{Nb} = r_{Ta} = 1.45$ kX).

With an increase of the Ta content in the solid solution, the melting point of the latter decreases, and for two-phase alloys, $Zr_{0.416}Ta_{0.584}C_{0.416}$–$Zr_{0.160}Ta_{0.840}C_{0.160}$, is 2750°K, which is 300° above
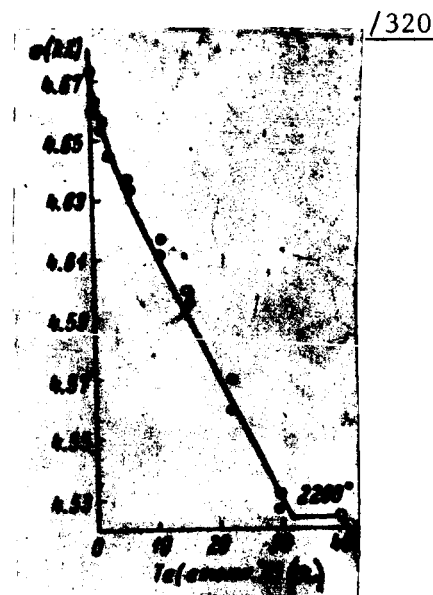


Figure 1. Dependence of the Lattice Constant on the Concentration of Ta in Solid Solution on the ZrC Base. Legend: a = Ta (Atomic %).

3

the melting point in two-phase ZrC-Nb alloys [3]. The maximum quantity of dissolving tantalum is attained at a given temperature and is about 35% (atomic). Therefore, according to the ZrC-Ta(Nb) profiles, at the temperatures of appear- <span>/321</span> ance of the liquid phase an equal quantity of metals of the group V-Nb and Ta is dissolved in a solid solution on the basis of ZrC. The characteristic structures of some alloys, whose composition lies on the ZrC-Ta profile, are given in Figure 2.
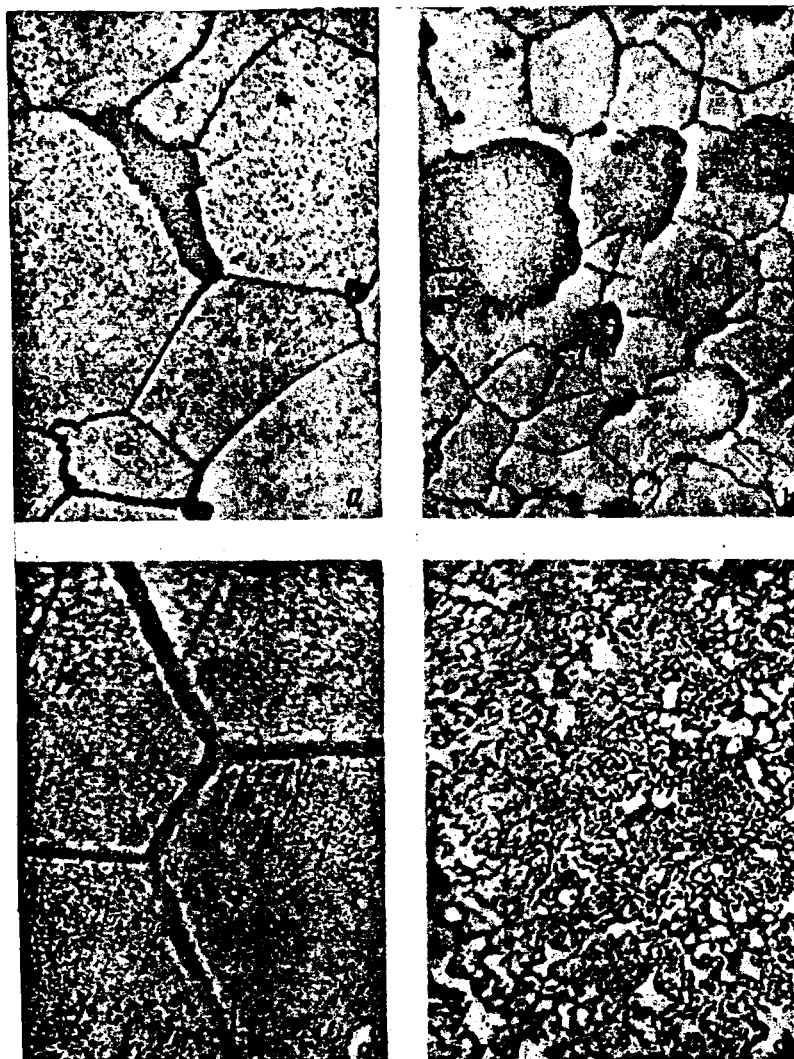


Figure 2. Structures of Some Alloys in the Zr-C-Ta System.

Legend:   a = $Zr_{0.633}Ta_{0.367}C_{0.633}$ (ZrC + 50% Ta); 2773°K, 1 hour; b = $Zr_{0.534}Ta_{0.436}C_{0.534}$ (ZrC + 60% Ta); 2473°K, 1 hour; c = $Zr_{0.534}$, $Ta_{0.436}C_{0.534}$ (ZrC + 60% Ta); 2773°K, 1 hour; d = $Zr_{0.301}Ta_{0.699}C_{0.301}$ (ZrC + 80% Ta); 2750°K, 3 minutes. Magnification, 800X.

A radiographic analysis of the alloys listed in Table 2 made it possible to establish that at 2273°K after a 6-hour exposure we had the two-phase alloys I, II, III, VIII, IX, X, and the three-phase alloys IV-VII, XI, XIII. The same <span>/322</span> as in the investigation of the structure of the alloys of the Zr-C-Nb system [3], in the construction of the Zr-C-Ta section (Figure 3) we took into account data on the structure of alloys of the Ti-C-Ta system [19], where the existence of the $(Ta, Ti)_2C$ phase is extremely limited.
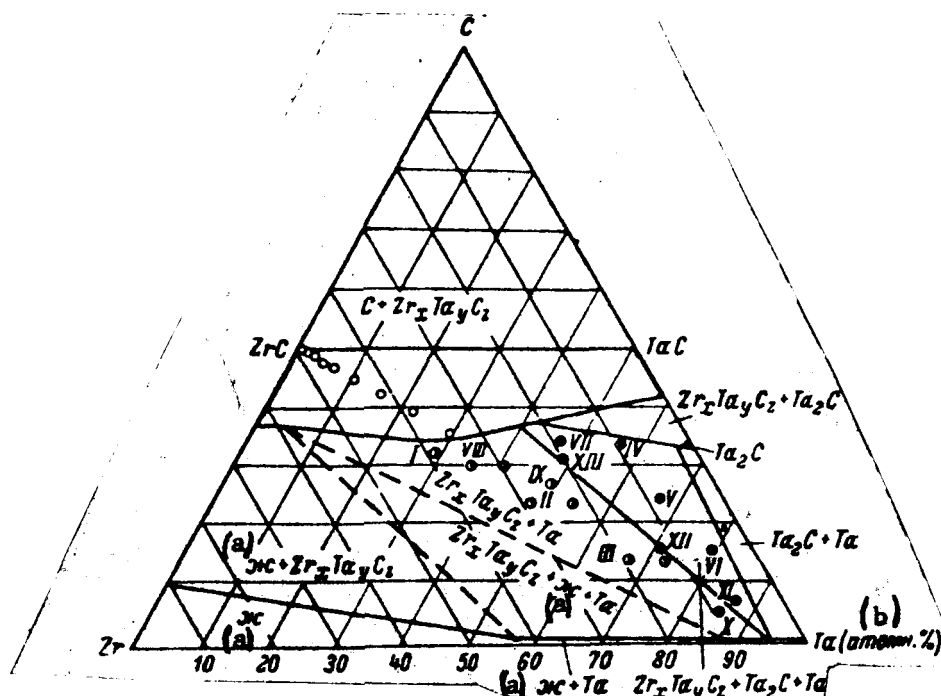


Figure 3. Isothermal Section at 2273°K of the Zr-C-Ta System. Legend: a = Liquid; b = Ta (Atomic %).

Taking into account the great difference of the atomic radii $r_{Zr}$ and $r_{Ta}$, we sharply limited the region of existence of solid solutions on a $Ta_2C$ base and the field of three-phase equilibrium was determined on the basis of a radiographic phase analysis in such a way that it intersects the ZrC-Ta profile, that is, indicates a non-quasi-binary character of the latter. This conclusion agrees with the data in [20], which gives an isothermal section of the Zr-C-Ta system at 1720°K. It can be seen from a comparison of the structure of isothermal sections at 1723 and 2273°K that the field of three-phase equilibrium $Zr_xTa_yC_z$ + $(Ta, Zr)_2C$ + $(Ta, Zr)$ almost does not change its position with an increase of temperature; there is only a change of the boundary of the nonstoichiometric complex carbides and a change of the phase fields; for example, the three-phase field $\beta-(Zr, Ta)$ + $Zr_xTa_yC_z$ + $(Ta, Zr)$ disappears. The two-phase field $Zr_xTa_yC_z$ + $(Ta, Zr)$ exists in a wide range of compositions and temperatures, which makes it possible to create on its basis important two-phase

5

alloys of the cermet type. The polythermal profile ZrC-Ta, constructed on this basis and on the basis of data on determination of the melting points of the alloys lying on this profile, is shown in Figure 4.
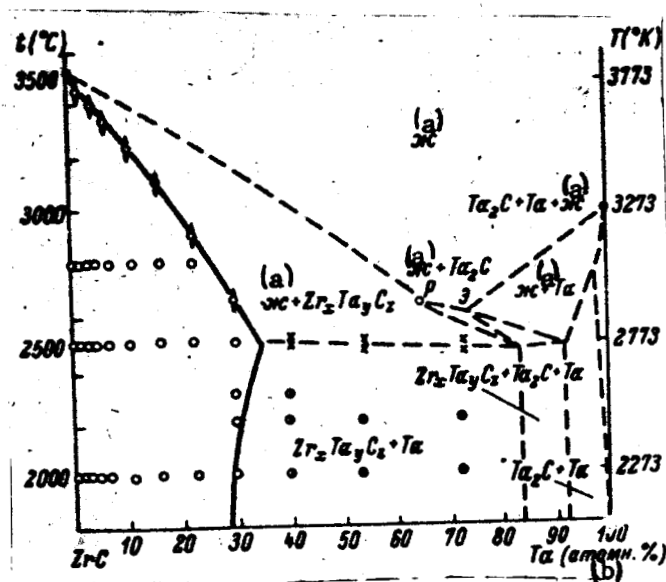


Figure 4. Polythermal ZrC-Ta Profile.
Legend: a = Liquid; b = Ta (Atomic %).

## CONCLUSIONS

1. An isothermal section at 2273°K and a ZrC-Ta polythermal section were constructed on the basis of data from radiographic, metallographic and chemical analyses and determination of the melting points of alloys of the Zr-C-Ta system and it was demonstrated that triple compounds do not exist in the system. In the solid state there are three single-phase fields -- $Zr_xTa_yC_z$, $(Ta, Zr)_2C$ and $(Ta, Zr)$; three two-phase fields -- $Zr_xTa_yC_z + (Ta, Zr)$, $(Ta, Zr) + (Ta, Zr)_2C$ and $(Ta, Zr)_2C + Zr_xTa_yC_z$; and the three-phase field -- $Zr_xTa_yC_z + (Ta, Zr)_2C + (Ta, Zr)$, that is, only phases existing in the corresponding double systems.

2. On the basis of the results in this study it can be assumed that in the mentioned system it is possible to create refractory alloys, both single-phase on the basis of cubic carbides, and two-phase cermets with metallic tantalum as a bond, melting at 2750°K.

6

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